

Interplay of superexchange and orbital degeneracy in Cr-doped LaMnO_3

Joachim Deisenhofer, Michalis Paraskevopoulos, Hans-Albrecht Krug von Nidda,
and Alois Loidl

*Experimentalphysik V, Elektronische Korrelationen und Magnetismus,
Institut für Physik, Universität Augsburg, D - 86159 Augsburg, Germany*

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We report on structural, magnetic and Electron Spin Resonance (ESR) investigations in the manganite system $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ ($x \leq 0.5$). Upon Cr-doping we observe a reduction of the Jahn-Teller distortion yielding less distorted orthorhombic structures. A transition from the Jahn-Teller distorted O' to the pseudocubic O phase occurs between $0.3 < x < 0.4$. A clear connection between this transition and the doping dependence of the magnetic and ESR properties has been observed. The effective moments determined by ESR seem reduced with respect to the spin-only value of both Mn^{3+} and Cr^{3+} ions.

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I. INTRODUCTION

It was recently shown that in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ the realization of an insulating and ferromagnetic ground state for $0.1 < x < 0.15$ results from a superexchange (SE) driven rearrangement of the high-temperature orbital order (OO) established by the Jahn-Teller (JT) distortion.^{1,2} Upon Sr-doping the JT distortion in the parent compound gets suppressed and the degeneracy of the Mn^{3+} e_g electrons becomes almost restored. In this case the two-orbital model by Kugel and Khomskii becomes valid and ferromagnetic SE interactions between Mn^{3+} ions show up.³ These drive the system into an orbitally ordered and ferromagnetic state. The exact nature of the OO is still unclear, although some proposals have been made by Khomskii recently,⁴ based on the idea of the so called orbital polaron by Kilian and Khaliullin.⁵ The realization of a ferromagnetic and insulating state has been recently addressed by Khomskii and Sawatzky⁶ and also by Mizokawa *et al.*⁷ For even higher Sr-doping levels ($x \geq 0.17$) the increasing double-exchange (DE) interactions become dominant and establish a ferromagnetic and metallic ground state.

Since the first studies of the series $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ in the fifties,^{8,9,10} it has been known that upon Cr-doping the antiferromagnetic Mott insulator LaMnO_3 develops a ferromagnetic component. Moreover, Taguchi *et al.* reported (for $T > 300$ K) that within the complete concentration range $0 \leq x \leq 1$ the samples show semiconducting behavior.¹¹ Sun *et al.* and Zhang *et al.* came to similar conclusions for the temperature range $T < 300$ K, recently.^{12,13} Due to the ceramic nature of the samples a direct comparison of the resistivity values of these studies is vain, but both yield an increase in resistivity with increasing Cr concentration (at fixed temperatures) indicating the persistence of an insulating ground state throughout the whole concentration range. Hence, the $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ system is a promising candidate for studying the close relationship between JT distortion, SE interactions and orbital degeneracy, especially because in the simple ionic picture the Mn^{3+} ($3d^4$) ions are partially

substituted by isoelectronic Cr^{3+} ions ($3d^3$), which have the same electronic configuration as Mn^{4+} (e.g. t_{2g}^3) in these compounds. Therefore no mobile charge carriers should be present in contrast to the Sr-doped case.

However, Sun *et al.* and Zhang *et al.* invoked the possibility of Mn^{3+} -O-Cr³⁺ double-exchange interactions in $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ in order to correlate their electronic transport data with the magnetic properties in their samples.^{12,13} Magnetoresistance measurements ($T > 77$ K) have been reported by Gundakaram *et al.* in the system $\text{LnMn}_{1-x}\text{Cr}_x\text{O}_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}$) indicating the absence of DE interactions.¹⁴

The influence of Cr-doping in mixed-valence manganites has been investigated by Cabeza *et al.* in the system $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$.¹⁵ Their conclusion, namely that the Cr-ions do not contribute to the DE mechanism, is in accordance with the observations of Kimura *et al.* and Troyanchuk *et al.*, who investigated the influence of Cr-doping in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ and $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$, respectively.^{16,17,18} In contrast, Sun *et al.* again found indications for DE in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$.¹⁹

In the present paper we try to shed some light on the controversial findings by comparing the influence of Cr-doping on the magnetic properties of LaMnO_3 with the intensively studied DE systems $\text{La}_{1-x}(\text{Ca}, \text{Sr})_x\text{MnO}_{3+\delta}$.

II. EXPERIMENTAL DETAILS

The polycrystalline specimens were prepared using conventional ceramic techniques. Ultra pure oxide powders (La_2O_3 (4N), Mn_2O_3 (4N) and Cr_2O_3 (4N), Alpha) were dried, mixed in the appropriate amounts and carefully ball-milled to ensure homogeneous samples. The $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 0.5$) samples have been pressed into pellets and were prepared by heating in flowing pure nitrogen at 1400°C for 120 hours and then slowly cooled to room temperature. This procedure was repeated four times. Powder diffraction patterns were collected employing $\text{Cu-K}_{\alpha 1}$ radiation at room temperature.

The magnetic susceptibility and magnetization were measured using a dc superconducting quantum interference device (SQUID) magnetometer ($0 - 50$ kOe, 1.5 K $\leq T \leq 400$ K).

ESR measurements were performed with a Bruker ELEXSYS E500 CW-spectrometer at X-band frequencies ($\nu \approx 9.35$ GHz) equipped with continuous gas-flow cryostats for He (Oxford Instruments) and N₂ (Bruker) in the temperature range between 4.2 K and 680 K. The polycrystalline samples were powdered and filled into quartz tubes and fixed with either paraffin (at low temperatures 4 K $\leq T \leq 300$ K) or NaCl (at 300 K $\leq T \leq 680$ K).

III. EXPERIMENTAL RESULTS

A. Structural properties

In Figure 1 we show the orthorhombic lattice parameters (a , b , c) as a function of the Cr-concentration x . All parameters show a linear dependence on x up to 0.3. A transition from the Jahn-Teller distorted O'-phase to the pseudocubic ($a \approx b \approx c/\sqrt{2}$) O-phase occurs between $0.3 < x < 0.4$. In the Jahn-Teller distorted phase the Mn-O bond lengths in the MnO₆ octahedra are highly anisotropic and become isotropic in the pseudocubic O phase. Our findings are in agreement with the structural data of Gundakaram *et al.*¹⁴ The authors also showed that the sample-preparation method described above ensures the absence of Mn⁴⁺ ions in these compounds confirmed by analysis of the samples via iodometric titration. Therefore we estimate the deviation from the ideal oxygen value to be less than 1%. The persistence of the orthorhombic structure up to $x = 0.5$ has also been reported by Nakazono *et al.*²⁰

Sun *et al.* reported that a transition from rhombohedral to orthorhombic symmetry occurs around $x = 0.2$.¹²

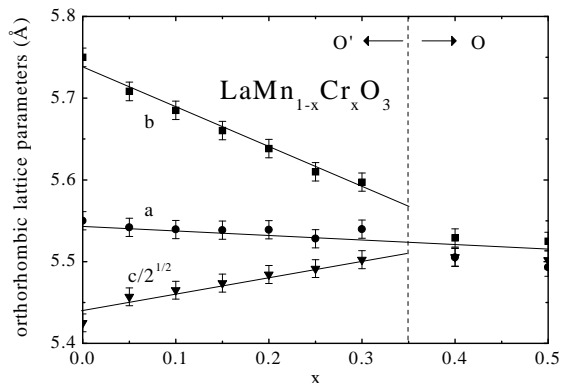


FIG. 1: Orthorhombic lattice parameters (a , b , c) as a function of Cr concentration x . A transition from the Jahn-Teller distorted O'-phase to the pseudocubic ($a \approx b \approx c/\sqrt{2}$) O-phase occurs between $0.3 < x < 0.4$. The lines are to guide the eyes

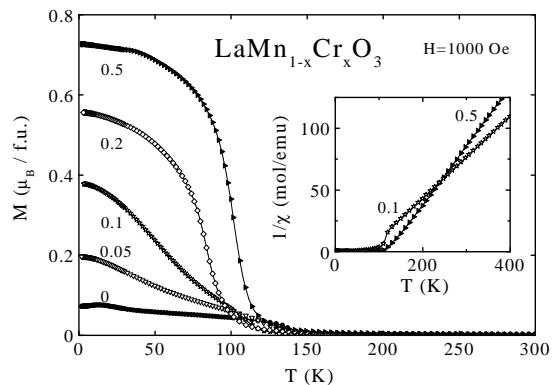


FIG. 2: Temperature dependence of the magnetization M with a applied field $H = 1000$ Oe. In the inset the inverse susceptibility *vs.* temperature is plotted for $x = 0.1$ and $x = 0.5$.

Since no detailed analysis of the lattice parameters and information about the atmosphere used in the preparation procedure was provided, it is difficult to argue where this discrepancy results from: A closer look on the X-ray-diffraction spectra presented by Sun *et al.* might reveal the persistence of the orthorhombic distortion or a mixed phase up to $x = 0.3$. The samples in the study by Zhang *et al.* ($x \leq 0.3$) reportedly were all found to exhibit rhombohedral symmetry,¹³ whereas Taguchi *et al.* found rhombohedral symmetry for $x \geq 0.4$ and orthorhombic for $x \leq 0.4$ and a high Mn⁴⁺ content due to oxygen non-stoichiometry.¹¹

It is known that if upon Sr-doping the percentage of Mn⁴⁺ in LaMnO₃ becomes larger than 20%, the room-temperature structure is rhombohedral.²¹ The influence of oxygen content on the structural properties has been intensively studied in LaMnO_{3+ δ} by Prado *et al.*,²² who found a rhombohedral structure at room temperature for an oxygen excess of $\delta > 0.09$, which corresponds to a Mn⁴⁺ content similar to a Sr concentration of $x = 0.18$. Therefore, it is possible that oxidation (*i.e.* oxygen non-stoichiometry) of the samples holds for the differences in the structural, electronic and magnetic properties.

Two main reasons account for the different behavior of Cr³⁺ and Mn⁴⁺ ions (both are not JT active): Firstly, the ionic radius of the Cr³⁺ ion is larger than the corresponding one of the Mn⁴⁺ ion and hence the destabilization of the Mn³⁺ Jahn-Teller matrix is weaker than in the Sr-doped samples. Additionally, the mobile nature of the induced charge carriers (holes) in the case of Sr-doping allows for a dynamical change of the local electronic configuration and a homogenous distribution of the Mn⁴⁺ ions in the JT matrix, whereas the Cr³⁺ ions are fixed to the lattice sites at the time of sample preparation.

FIG. 4: Field dependence of the dc-magnetization M at $T = 5$ K. Inset: spontaneous magnetization M_s as a function of Cr-doping.

component upon increasing Cr-doping is clearly evident. Additionally, upon increasing Cr concentration the samples become magnetically softer, as indicated by the decreasing coercive fields in the hysteresis loops. As shown in the inset of Figure 4, the spontaneous magnetization M_s (obtained by extrapolation from the data at the highest magnetic fields, see lower panel of Fig. 4) increases linearly with the concentration of Cr^{3+} and reaches a maximum at $x = 0.3$. In the O-phase M_s shows a constant behavior, similar to p_{eff} and Θ .

In principle, the behavior of the magnetic parameters discussed above is in accordance with the early studies by Jonker and Bents.^{8,9}

C. Electron Spin Resonance

Electron spin resonance detects the power P absorbed by the sample from the transverse magnetic microwave field as a function of the static magnetic field H . The signal-to-noise ratio of the spectra is improved by recording the derivative dP/dH with lock-in technique. ESR spectra, which are characteristic for the paramagnetic regime, are presented in Fig. 5, illustrating their evolution with Cr concentration x (left column) and temperature T (right column). Within the whole paramagnetic regime the spectrum consists of a broad, exchange narrowed resonance line, which is well fitted by a Lorentzian line shape as described previously.²³

The integrated intensity $I(T)$ of the resonance line

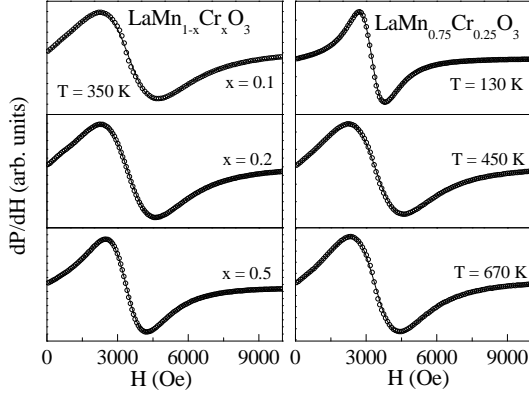


FIG. 5: ESR spectra of $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$. Left column: various Sr concentrations x at $T = 350$ K. Right column: temperature evolution of the ESR spectrum for $x = 0.25$. Solid lines represent the fits using the Lorentzian line shape.

measures the spin susceptibility χ_{ESR} of the ESR probe. For ferromagnetically coupled ions its temperature dependence usually follows a CW law, where Θ is the CW temperature. Indeed, we observed a linear behavior of $1/I(T)$ in the paramagnetic regime within the whole concentration range. The CW temperatures as determined from the ESR experiments agree well with values obtained from susceptibility measurements (Fig. 3(b)). By comparison with the intensity of the reference compound $\text{Gd}_2\text{BaCuO}_5$,²⁴ we obtained the effective moments, which are in good agreement with the magnetic susceptibility data except for $x = 0.5$.

In the non-JT distorted orthorhombic O phase ($x = 0.4$) the resonance field H_{res} yields an effective g value $g_{\text{eff}} \approx 1.99$ slightly below the free-electron value, which is characteristic for transition-metal ions with a less than half filled d-shell.²⁵ In Fig. 6 we show $\Delta H_{\text{res}} = H_{\text{res}}(T) - H_{\text{res}}(670\text{K})$ for concentrations $x \geq 0.15$. At 670 K the resonance fields for these samples reach values characteristic for the O phase $H_{\text{res}}(670\text{K}) \approx 3.34$ kOe. For $x < 0.15$ the resonance shift is even larger, but the structural phase transition seems to take place beyond our accessible temperature range. However, the resonance shift at $T = 400$ K for $x \geq 0.15$ (see inset of Fig. 6) clearly mirrors the structural phase transition as the shift decreases with increasing Cr concentration and drops to almost zero for $x \geq 0.4$.

Finally approaching the ordering temperature from above, the whole resonance becomes seriously distorted and is strongly shifted to lower fields due to the internal fields caused by the onset of magnetic order. A similar evolution of the resonance line has been reported by Sun *et al.* and interpreted as an indication for DE.¹² However, we restrict our discussion to the paramagnetic phase ($T > T_N$), because in order to characterize the magnetic order accurately one needs single-crystals of de-

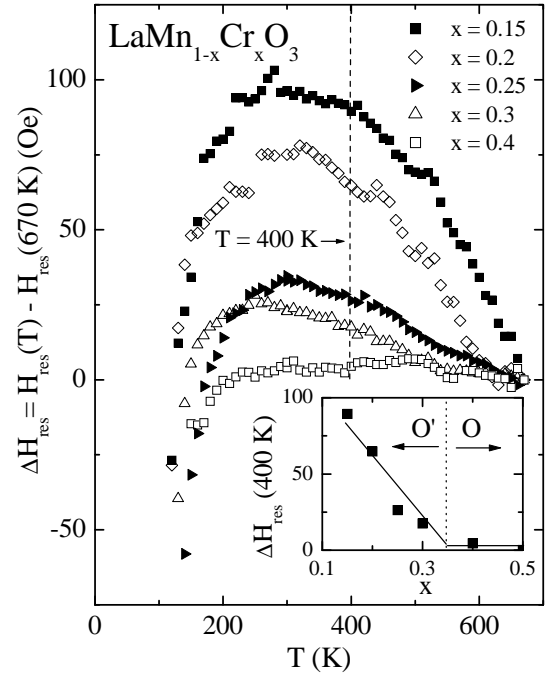


FIG. 6: Temperature dependence of the resonance shift $\Delta H_{\text{res}} = H_{\text{res}}(T) - H_{\text{res}}(670\text{K})$ for $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ ($x \geq 0.15$). Inset: Resonance shift at 400 K as a function of Cr-doping.

finer shape instead of randomly oriented powder which gives rise to the observed distortion of the lineshape.

Figure 7 shows the characteristic temperature dependence of the ESR linewidth. All samples with $x \leq 0.3$ show a broad maximum in the JT distorted phase and a minimum above the critical broadening on approaching magnetic order. For the parent compound LaMnO_3 the maximum cannot be detected within the investigated temperature range, but has been reported by Causa *et al.*²⁶ For the highest temperatures under investigation the linewidth of all samples with $x > 0.05$ seem to converge indicating the range of the high-temperature limit. For $x > 0.3$ the maximum is not observable anymore and the linewidth shows a monotonous increase with increasing temperatures. The inset of Fig. 7 shows the dependence of the linewidth at 450 K on the Cr concentration. At this temperature the samples with $x \leq 0.3$ reveal the broad maximum, but have not yet reached the high-temperature limit. The obvious jump at the critical concentration reflects the transition from the O'- to the O-phase (Fig. 1) thus revealing a close correlation between spin relaxation and structural distortion.

IV. DISCUSSION

A. ESR linewidth and resonance field

The temperature dependence of the linewidth and the resonance field of $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ for $x \leq 0.3$ is very

If the external field is applied within the ferromagnetically coupled ab -plane, the linewidth reveals a broad maximum within the JT distorted O' phase, whereas ΔH is nearly constant, if the external field is parallel to the antiferromagnetically coupled c -axis. We also investigated a powdered $\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$ sample and found that the linewidth shows the same features as the single crystal for the external field applied within the ab -plane. Correspondingly, we observed a resonance shift to higher magnetic fields within the JT distorted O' phase, when the external field is within the ab -plane, and a constant behavior along the c -axis. In our recent approach we presented a detailed analysis for the angular dependence of the linewidth and the resonance field in $\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$ in the O' phase by taking into account the crystal field (CF) and the Dzyaloshinsky-Moriya (DM) interaction,²⁸ which were shown to yield by far the largest contribution to the linewidth in manganites by Huber *et al.*²⁹ Due to the similarities in the temperature dependence of ΔH and H_{res} we assume that these two interactions also account for the ESR properties in Cr-doped LaMnO_3 .

Unfortunately, in the case of polycrystalline samples such a detailed analysis is not possible due to the random orientation of the powder. However, a similar behavior of ΔH vs. T has also been reported in polycrystalline $\text{LaMnO}_{3+\delta}$ by Tovar *et al.*,³⁰ who found a broad linewidth maximum in the O' phase up to $\delta = 0.04$. The corresponding JT transition temperatures decrease from 700 K for $\delta = 0$ to 400 K for $\delta = 0.05$, and for $\delta > 0.05$ the cooperative JT distortion vanishes concomitantly with the broad maximum. The authors describe the temperature dependence of the exchange-narrowed linewidth by following Huber *et al.* as

$$\Delta H(T) = \frac{\chi_0(T)}{\chi(T)} \Delta H_\infty \quad (1)$$

with the free Curie susceptibility $\chi_0 \propto T^{-1}$ and the static susceptibility $\chi(T) \propto (T - \Theta)^{-1}$.²⁹ The high-temperature linewidth ΔH_∞ depends on the contributions of both the CF and the DM interaction. Thus, we fitted the linewidth data for all samples under investigation by using eq. 1 (see Fig. 7), which can neither describe the critical broadening of the linewidth in the vicinity of a magnetic transition nor the structural transition at T_{JT} , but fits very nicely in between these transitions. The obtained parameters Θ and ΔH_∞ are shown in Fig. 8. Though the obtained CW temperatures are, in comparison with the values in Fig. 3b, slightly lower for $x \leq 0.3$ (O' phase) and enhanced for $x > 0.3$ (O phase), the overall tendency is the same. Moreover ΔH_∞ shows the same behavior as the linewidth values taken at 450 K (see inset of Fig. 7), confirming that the maximum linewidth is a good measure for the strength of the interactions.

The difference in ΔH_∞ observed between the O' and the O-phase is due to the fact that concomitantly with the disappearance of the cooperative JT effect the contribution of the single-ion anisotropy of the CF vanishes

FIG. 8: Doping dependence of the CW temperature Θ and ΔH_∞ obtained by fitting with eq. 1, the solid lines are to guide the eyes.

at T_{JT} whereas the DM contribution is due to the tilting of the octahedra, which for LaMnO_3 has been shown to remain nearly unchanged through the transition.^{31,32}

The obtained values in both phases are in agreement with those reported for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{LaMnO}_{3+\delta}$ of $\Delta H_\infty \approx 2.7$ kOe for the O'-phase and $\Delta H_\infty \approx 2.2$ kOe for the O phase yielding values of the order of 1 K for both interaction.^{29,30}

The influence of DE on the ESR linewidth in the paramagnetic regime is not fully understood and still subject of controversial discussion: Shengelaya *et al.* found that in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, where the cooperative JT distortion is already suppressed, the temperature dependence of the linewidth correlates with the conductivity and both parameters can be described by a small-polaron hopping model $\sim 1/T \exp(-E_a/k_B T)$ with similar activation energies E_a .³³ In contrast, in the optimally doped region $x = 0.33$ the linewidth has been described previously by eq. (1) only.^{34,35} Some authors argue that due to the different time scales the DE interaction, which manifests itself in the paramagnetic phase through the hopping of the JT polaron, cannot have any effect on the spin relaxation.^{29,36} However, we want to emphasize that in our case the linewidth can be satisfactorily described without any additional relaxation process connected to polaron hopping.

B. Magnetic Properties and ESR intensity

Though all observed parameters show a close correlation to the structural changes induced upon Cr-doping, the origin of the observed ferromagnetic component of the magnetization cannot easily be explained. From the values of the high-field magnetization (5 T) we deduce that the magnetic phase is not purely ferromagnetic, since the deviation from the theoretical values of $3 - 4\mu_B/\text{f.u.}$ for the full magnetic moment of all Mn^{3+} and Cr^{3+} spins cannot be attributed to temperature induced disorder, only. Therefore, we have to consider all exchange interactions between the Mn^{3+} and Cr^{3+} ions that could contribute to the magnetic state of the system:

In the parent compound LaMnO_3 the JT distortion lifts the degeneracy of the e_g orbitals and the Mn^{3+} -O - Mn^{3+} SE interaction yields antiferromagnetic coupling along the c -axis and ferromagnetic coupling in the ab -plane. In the case of degenerated e_g orbitals, the Kanamori-Goodenough rules³⁷ do not apply and the two-orbital Kugel-Khomskii model yields a purely ferromagnetic Mn^{3+} -O - Mn^{3+} SE interaction.³ Due to the weakening of the JT distortion upon Cr-doping, the degeneracy of the e_g orbitals can become almost restored (similar to the ferromagnetic insulating state of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) and favor ferromagnetism (FM). Taking into account the Kanamori-Goodenough rules³⁷ the Mn^{3+} -O - Cr^{3+} superexchange is ferromagnetic and therefore can also account for the increasing values of Θ in the O'-phase with increasing Cr-doping. Correspondingly, the anti-

ferromagnetic Cr^{3+} -O - Cr^{3+} superexchange should contribute considerably with increased Cr content and could account for the stabilization of the magnetic state for $x > 0.3$, where the observed parameters become almost constant. Finally, a DE interaction between Mn^{3+} -O - Cr^{3+} ions has been proposed.^{12,13}

Regarding the existence of DE, we can compare our data to observations of Prado *et al.*²² in $\text{LaMnO}_{3+\delta}$, where one can clearly see the impact of Mn^{4+} -O - Mn^{3+} double exchange on the magnetic properties: Though the hysteresis loops show a similar behavior upon increasing oxygen surplus as upon Cr-doping, the magnetic phase transition from AFM to FM at $\delta \approx 0.04$ is characterized by the appearance of the full magnetic moment of $3 - 4\mu_B/\text{f.u.}$ These features are also found upon doping with Sr.² How difficult it is to distinguish the involved interactions from the dc magnetization data only can be seen in comparison with the behavior of M vs. x in electron doped $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$,³⁸ which looks very similar to our system. However, this behavior has been found to correlate with the electron mobility and attributed to the dynamical charge transfer due to DE interactions. As neither such correlations nor the appearance of the full magnetic moment has been observed in $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$, we will consider the influence of DE in the following as negligible.

Due to the delicate interplay of the above SE interactions, Jonker favored the existence of a complex ferrimagnetism (FiM),⁹ and Bents found in his neutron diffraction study that not only FM, but also A-type AFM (for $x \leq 0.15$) and G-type AFM (for $x > 0.3$) are present in the system.⁸ A theoretical density-functional study by Yang *et al.* based on the data of these early publications supports the idea of FiM on account of positive Mn^{3+} -O - Mn^{3+} and negative Cr^{3+} -O - Cr^{3+} superexchange interactions. However, positive Mn^{3+} -O - Cr^{3+} interaction has not been found in the calculations.³⁹ Very recently, Ono *et al.* suggested another scenario based on their soft X-ray magnetic circular dichroism experiments.^{40,41} They found that the Mn ions are aligned parallel to the direction of the magnetization, whereas the Cr magnetization seems to disappear. In order to simulate such a behavior by using the Monte Carlo method, they had to assume a negative Mn^{3+} -O - Cr^{3+} interaction in contrast to the Kanamori-Goodenough rules. Assuming antiferromagnetic Mn^{3+} -O - Cr^{3+} superexchange the latter authors explain the cluster-glass-like behavior of the system as a frustration of the spins due to the competing SE interaction.²⁰ Although the reasons for the disappearance of the Cr magnetization are rather unclear, such a scenario is in accordance with the observed values of the spontaneous magnetization M_S values (see inset of Fig. 4): The linear increase in the JT distorted O' phase can be attributed to the partially restored degeneracy of the e_g orbitals,³ weakening the antiferromagnetic Mn^{3+} -O - Mn^{3+} SE (along the c -axis) and finally yielding only ferromagnetic Mn^{3+} -O - Mn^{3+} interaction for $x > 0.3$. Thus, the theoretical values of $1.6 - 2 \mu_B/\text{f.u.}$ are in agree-

ment with our data.

Astonishingly, we also observe that in contrast to Ca/Sr-doped LaMnO_3 , where the ESR signal has been attributed to both Mn^{3+} and Mn^{4+} ions,^{23,34} the ESR signal in the paramagnetic regime seems to be originated by the Mn^{3+} ions only (see Fig. 3): The effective moments determined by ESR follow the theoretical curve for Mn^{3+} up to $x = 0.5$ very nicely. The corresponding values from the magnetization measurements, however, are slightly enhanced in comparison to the ESR data, but the overall tendency is similar. In contrast to the SQUID measurements (see inset of Fig. 2), the ESR experiments were performed up to 670 K allowing a more reliable determination of the effective moments. Thus, the frustration of the Cr^{3+} ions even seems to influence the paramagnetic phase.

V. CONCLUSIONS

We presented a detailed magnetic analysis of the doping effect of Cr on LaMnO_3 . The parent compound is an A-type AFM with orbital order induced by a strong JT effect due to the double degeneracy of the e_g -orbitals of the Mn^{3+} ions. Upon doping with Cr^{3+} ions, ferromagnetic interactions show up. The magnetically ordered state can be understood in terms of a competition of positive Mn^{3+} -O- Mn^{3+} and negative Mn^{3+} -O- Cr^{3+} and Cr^{3+} -O- Cr^{3+} SE interactions. Assuming the disappearance of the Cr magnetization the increasing ferromagnetic component can be ascribed to the Mn^{3+} ions the

partial restoration of the double degeneracy of the e_g -orbitals due to the weakening of the JT matrix by non-JT active Cr^{3+} -ions. Additionally, the Jahn-Teller driven orbital order becomes weaker and finally disappears for doping levels between 0.3 and 0.4. All parameters, *i.e.* Θ , H_{res} and ΔH , reflect this transition in their doping dependence. Thus, the system can be considered as a ferromagnetic insulator with respect to Mn^{3+} in the sense of the two-orbital Kugel-Khomskii model, as the competing negative SE interactions seem to produce a disappearance of the Cr magnetization. The ESR properties can be naturally explained by the structural disorder induced upon Cr-doping and the effects of the CF and DM interactions. Moreover, the Cr^{3+} ions seem not to contribute to the ESR signal. From our experimental data we do not see any need to invoke the possibility of DE interaction between Cr and Mn ions. The questions about the origin of the disappearance of the Cr magnetization and why the Cr^{3+} ions seem to be ESR-silent remain unsolved problems and challenge further experimental and theoretical investigations.

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- ¹ Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Murakami, A. Nishizawa, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko, and S. Maekawa, *Phys. Rev. Lett.* **82**, 4328 (1999).
 - ² M. Paraskevopoulos, F. Mayr, J. Hemberger, A. Loidl, R. Heichele, D. Maurer, V. Müller, A. A. Mukhin, and A. M. Balbashov, *J. Phys.: Condens. Matter* **12**, 3993 (2000).
 - ³ K. I. Kugel and D. I. Khomskii, *Usp. Fiz. Nauk.* **136**, 621, (1982), [*Sov. Phys. Usp.* **25**, 231, (1982)].
 - ⁴ D. I. Khomskii, *Int. J. Mod. Phys. B* **15**, 2665 (2001).
 - ⁵ R. Kilian and G. Khaliullin, *Phys. Rev. B* **60**, 13 458 (1999).
 - ⁶ D. I. Khomskii and G. A. Sawatzky, *Solid State Commun.* **102**, 87 (1997).
 - ⁷ T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. B* **63**, 0244035 (2000).
 - ⁸ U. Bents, *Phys. Rev.* **106**, 225 (1957).
 - ⁹ G. H. Jonker, *Physica* **22**, 707 (1956).
 - ¹⁰ M. A. Gilleo, *Acta Crystallogr.* **10**, 161 (1957).
 - ¹¹ H. Taguchi, S. Matsu-ura, M. Nagao, and H. Kido, *Physica B* **270**, 325 (1999).
 - ¹² Y. Sun, W. Tong, X. Xu, and Y. Zhang, *Phys. Rev. B* **63**, 174438 (2001).
 - ¹³ L. W. Zhang, G. Feng, H. Liang, B. S. Cao, Z. Meihong, and Y. G. Zhao, *J. Magn. Magn. Mat.* **219**, 506236 (2000).
 - ¹⁴ R. Gundakaram, A. Arulraj, P. V. Vanitha, C. N. R. Rao, N. Gayathri, A. K. Raychaudhuri, and A. Cheetham, *J. Solid State Chem.* **127**, 354 (1996).
 - ¹⁵ O. Cabeza, M. Long, C. Severack, M. A. Bari, C. M. Muirhead, M. G. Francesconi, and C. Greaves, *J. Phys.: Condens. Matter* **11**, 2569 (1999).
 - ¹⁶ T. Kimura, R. Kumai, Y. Okimoto, Y. Tomioka, and Y. Tokura, *Phys. Rev. B* **62**, 15 021 (2000).
 - ¹⁷ T. Kimura, Y. Tokura, R. Kumai, Y. Okimoto, and Y. Tomioka, *J. Appl. Phys.* **89**, 6857 (2001).
 - ¹⁸ I. O. Troyanchuk and M. V. Bushinsky, V. V. Eremenko, V. A. Sirenko, H. Szymczak, *Fiz. Nizk. Temp.* **28**, 61, (2002), [*Low Temp. Phys.* **28**, 45, (2002)].
 - ¹⁹ Y. Sun, X. Xu, and Y. Zhang, *Phys. Rev. B* **63**, 054404 (2000).
 - ²⁰ S. Nakazono, K. Ono, and M. Oshima, *J. Magn. Magn. Mat.* **226-230**, 866 (2001); private communication.
 - ²¹ A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 14 103 (1995).
 - ²² F. Prado, G. Alejandro, R. D. Sánchez, A. Caneiro, M. T. Causa, and M. Tovar, *J. Solid State Chem.* **146**, 418 (1999).
 - ²³ V. A. Ivanshin, J. Deisenhofer, H.-A. Krug von Nidda,

- A. Loidl, A. A. Mukhin, A. M. Balbashov, and M. V. Eremin, Phys. Rev. B **61**, 6213 (2000).
- ²⁴ G. G. Goya, R. C. Mercader, L. B. Steren, R. D. Sanchez, M. T. Causa, and M. Tovar, J. Phys.: Condens. Matter **8**, 4529 (1996).
- ²⁵ A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, (Clarendon, Oxford, 1970).
- ²⁶ M. Causa, G. Alejandro, R. Zysler, F. Prado, A. Caneiro, and M. Tovar, J. Magn. Magn. Mat. **196-197**, 506 (1999).
- ²⁷ G. Alejandro M. T. Causa, C. A. Ramos, M. Tovar, and J. Fontcuberta, J. Magn. Magn. Mat. **226-230**, 2002 (2001).
- ²⁸ J. Deisenhofer, M.V. Eremin, D. V. Zakharov, V. A. Ivanshin, R. M. Eremina, H.-A. Krug von Nidda, A. A. Mukhin, A. M. Balbashov, and A. Loidl, Phys. Rev. B **65**, 104440 (2002).
- ²⁹ D. L. Huber, G. Alejandro, A. Caneiro, M. T. Causa, F. Prado, M. Tovar, and S. B. Oseroff, Phys. Rev. B **60**, 12 155 (1999).
- ³⁰ M. Tovar, G. Alejandro, A. Butera, A. Caneiro, M. T. Causa, F. Prado, and R. D. Sanchez, Phys. Rev. B **60**, 10 199 (1999).
- ³¹ Q. Huang, A. Santoro, J. W. Lynn, R. W. Erwin, J. A. Borchers, J. L. Peng, and R. L. Greene, Phys. Rev. B **55**, 14 987 (1997).
- ³² M. v. Zimmermann, C.S. Nelson, Y.-J. Kim, J.P. Hill, Doon Gibbs, H. Nakao, Y. Wakabayashi, Y. Murakami, Y. Tokura, Y. Tomioka, T. Arima, C.-C. Kao, D. Casa, C. Venkataraman, Th. Gog, Phys. Rev. B **64**, 064411 (2001).
- ³³ A. Shengelaya, Guo-meng Zhao, H. Keller, K. A. Müller, and B. I. Kochelaev, Phys. Rev. B **61**, 5888 (2000).
- ³⁴ M.T. Causa, M. Tovar, A. Caneiro, F. Prado, G. Ibañez, C.A. Ramos, A. Butera, B. Alascio, X. Obradors, S. Piñol, F. Rivadulla, C. Vázquez-Vázquez, A. López-Quintela, J. Rivas, Y. Tokura, and S.B. Oseroff, Phys. Rev. B **58**, 3233 (1998).
- ³⁵ S.B. Oseroff, M. Torikachvili, J. Singley, S. Ali, S.-W. Cheong, and S. Schultz, Phys. Rev. B **53**, 6521 (1996).
- ³⁶ F. Rivadulla, M.T. Causa, L.E. Hueso, A. Fondado, J. Rivas, and M.A. Lopez-Quintela, Physica B **284-288**, 1418 (2000).
- ³⁷ J.B. Goodenough, *Magnetism and the Chemical Bond*, (Interscience, New York, 1963).
- ³⁸ J.J. Neumeier and J.L. Cohn, Phys. Rev. B **61**, 14 319 (2000).
- ³⁹ Z. Yang, L. Ye, and X. Xie, J. Phys.: Condens. Matter **12**, 2737 (2000).
- ⁴⁰ K. Ono, S. Nakazono, T. Kihara, Y. Nakamura, M. Miyayama, H. Fujioka, M. Oshima, and T. Koide, Physica B **284-288**, 1420 (2000).
- ⁴¹ K. Ono, S. Nakazono, and M. Oshima, J. Magn. Magn. Mat. **284-288**, 869 (2001).